New Type of Wave Function for Li, Be^+, and B^{++}†

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A recently developed method for electronic wave functions has been applied to Li, Be^+, and B^{++}. This method, the G1 method, leads to much better energies than does the Hartree-Fock (HF) method (for Li the G1 energy is −7.447560 as compared to the HF energy of −7.432727); however, *the independent-particle interpretation is retained.* A significant difference is that although the HF valence orbital has a node (being orthogonal to the core orbital), none of the three G1 orbitals has a node. The valence G1 orbital satisfies the cusp condition at the nucleus, has a minimum in the core region, and outside the core region is very similar to the HF valence orbital. The G1 wave function has the form of a paired-electron wave function but strong orthogonality is *not* imposed. Since the resulting orbitals have significant overlaps and since the energy is made much worse by imposing strong orthogonality, it appears that strong orthogonality is a significant constraint for orbital-type paired-electron wave functions (such as in the extended valence bond method). Since the G1 wave function is nearly at the radial limit and does not include instantaneous correlation among the electrons, the dynamic correlation is essentially all due to angular correlation just as for two electron atoms and ions. Since the G1 valence orbitals need not be orthogonal to the core orbitals, the use of this method for solids could eliminate these problems in band-structure calculations which are due to the orthogonality conditions inherent in the HF method.

I. INTRODUCTION

OUR conceptual foundation for understanding atoms has been the Hartree-Fock (HF) method. In this method the wave function is approximated as a Slater determinant[1] of spin orbitals, and each orbital is determined as the optimum state for an electron moving in the self-consistent field due to other electrons. The resulting orbitals are orthogonal and each can hold up to two electrons (one of each spin) and is taken as an eigenfunction of $\hat{l}^2$ and $\hat{l}_z$. One can derive a somewhat universal energy ordering of the orbitals for atoms and develop an Aufbau scheme which for nontransition elements usually leads to the correct ground configurations and the correct ordering of the low excited configurations, and thus explains the periodic relationships among the elements. Because of these beautiful qualitative successes, we have no right to quibble with the HF method if there should be some properties for which it leads to a few percent error.

However, there are some well-known deficiencies[2] with this method when applied to molecules, such as the bad dissociation as the molecule is pulled apart. And even for atoms there are some problems. One is that the HF method usually leads to incorrect spin densities at the nucleus. Another is that for many stable negative ions the HF wave function leads to a higher energy for the ion than for the atom.

A crucial feature leading to the interpretive successes of the HF method is that it leads to an independent-particle interpretation. That is, the many-electron wave function can be interpreted in terms of orbitals, each of which is an eigenstate of an electron moving in the (self-consistent) field due to the other electrons. An important question here is whether the HF method is the *best* one leading to an independent-particle interpretation and if not whether the others remove the deficiencies of the HF method and yet lead to successful Aufbau pictures.

It has now been shown[2] that one *can* go beyond the HF method and yet retain the independent-particle interpretation while removing such problems as improper molecular dissociation,[2,3] bad description of negative ions,[4] and poor spin densities at nuclei.[5] In addition, the new method, the GI method, apparently leads to a satisfactory Aufbau principle.

The next question is whether the new method through its independent-particle interpretation leads to any significant changes in our concepts of, say, atoms. The three-electron wave functions reported here are examined from this point of view, and even for this simple case some modifications in concepts are in order.

II. G1 METHOD

The general GI method for electronic wave functions has been described elsewhere.[2] There are two important special cases of the GI method, the G1 method and the GF method. The GF method has been described elsewhere[2,6] and applied to several systems including H_2[2], LiH[2], He[4], Li[4], Be[4], Li_2[3], CH_4[3], and CH_3[3].

For the case of three electrons the G1 wave function is

$$G_1{}^{\mu}(\phi_{1a}(1)\phi_{1b}(2)\phi_{2a}(3)\alpha(1)\beta(2)\alpha(3)), \qquad (1)$$

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[1] A linear combination of determinants is sometimes required in order to obtain the correct symmetry, but a single determinant is always sufficient for closed-shell and half-closed-shell systems.
[2] W. A. Goddard, III, Phys. Rev. **157**, 81 (1967), hereafter called II.
[3] W. A. Goddard, III, J. Chem. Phys. (to be published), hereafter called IV.
[4] W. A. Goddard, III, J. Chem. Phys. **48**, 1008 (1968).
[5] W. A. Goddard, III, Phys. Rev. **157**, 93 (1967).
[6] W. A. Goddard, III, J. Chem. Phys. (to be published), hereafter called III.

TABLE I. Basis sets and results for G1 calculations on Li, Be^+, and B^{++}. (Hartree atomic units are used.[a])

	Li *a3*	Li *b4*	Li *c6*	Li *d5*	Li *e6*	Li *f6*	Li *g6*	Li *h7*	Be^+ *i6*	B^{++} *j6*
	1s 3.788	1s 3.786	1s 5.29	1s 3.0	1s 3.0	1s 3.0	1s 2.993	1s 3.0	1s 4.0	1s 5.0
	1s 2.2815	1s 2.3190	2s 5.29	3s 4.32	3s 4.31	4s 5.35	4s 5.43	4s 5.33	4s 6.87	4s 7.86
	2s 0.6545	3s 3.751	1s 2.395	3s 3.069	3s 3.094	3s 4.79	3s 4.78	3s 5.4	3s 6.87	3s 7.86
		2s 0.6547	2s 2.395	3s 1.341	3s 1.369	3s 2.989	3s 2.979	3s 2.999	3s 4.04	3s 4.84
			1s 0.6727	3s 0.7803	3s 0.842	3s 1.293	3s 1.295	3s 1.347	3s 2.002	3s 2.702
			2s 0.6727		4s 0.707	3s 0.7695	3s 0.7693	3s 0.841	3s 1.327	3s 1.875
								4s 0.732		
E	−7.446137	−7.447267	−7.447553	−7.447531	−7.447540	−7.447556	−7.447556	−7.447560	−14.29162	−23.38990
$V/2E$	1.000002	0.999978	0.999998	0.999859	0.999856	1.000011	1.000001	1.000001	1.000002	1.000000
Cusps	−3.5351	−3.1555	−2.9009	−3.0000	−3.0000	−3.0000	−2.993	−3.0000	−4.0000	−5.0000
	−1.6205	−2.7666	−3.2109	−3.0000	−3.0000	−3.0000	−2.993	−3.0000	−4.0000	−5.0000
	−3.7007	−2.2346	−3.2294	−3.0000	−3.0000	−3.0000	−2.993	−3.0000	−4.0000	−5.0000
$\langle \Sigma \delta(r_i) \rangle$	13.722	13.903	13.870	13.837	13.839	13.865	13.854	13.864	35.139	71.501
$Q(0)$	0.2152	0.2204	0.2076	0.2095	0.2091	0.2097	0.2094	0.2095	0.9467	2.431
$\langle \Sigma r^2 \rangle$	19.077	19.039	18.619	18.607	18.663	18.624	18.634	18.654	6.5592	3.4135
ϵ_{1a}	−2.8378	−2.8397	−2.8426	−2.8424	−2.8425	−2.8426	−2.8427	−2.8427	−5.4892	−9.0661
ϵ_{1b}	−2.4638	−2.4549	−2.4587	−2.4586	−2.4587	−2.4587	−2.4588	−2.4588	−5.0457	−8.5736
ϵ_{2a}	−0.19589	−0.19596	−0.19615	−0.19614	−0.19615	−0.19615	−0.19615	−0.19615	−0.66589	−1.3895
$\phi_{1a}(0)$	3.567	3.389	3.337	3.361	3.361	3.353	3.351	3.352	5.163	7.200
$\phi_{1b}(0)$	1.551	1.757	1.805	1.774	1.775	1.788	1.788	1.789	3.027	4.479
$\phi_{2a}(0)$	0.1041	0.09341	0.09524	0.09404	0.09437	0.09357	0.09352	0.09366	0.2258	0.3846

[a] See Ref. 10.

where ϕ_{1a}, ϕ_{1b}, ϕ_{2a} are orbitals which are self-consistently optimized with respect to each other, α and β are the spin-up and spin-down eigenfunctions of $\hat{s}_z$, and[7,8]

$$G_1{}^\mu = O_{11}{}^\mu \omega_{1\bar{1}}{}^\mu - O_{21}{}^\mu \omega_{2\bar{1}}{}^\mu , \tag{2}$$

$$O_{11}{}^\mu = \tfrac{1}{6}[2e-(123)-(132)+2(12)-(13)-(23)],$$
$$O_{21}{}^\mu = \tfrac{1}{6}\sqrt{3}[-(123)+(132)-(13)+(23)],$$
$$\omega_{1\bar{1}}{}^\mu = \tfrac{1}{6}[2e-(123)-(132)-2(12)+(13)+(23)], \tag{3}$$
$$\omega_{2\bar{1}}{}^\mu = \tfrac{1}{6}\sqrt{3}[(123)-(132)-(13)+(23)],$$

where O^μ and ω^μ are Wigner projection operators based on the orthogonal representation[9] for the symmetric group. Here O^μ operators on spatial coordinates, ω^μ operates on spin coordinates (the tableaux are given in Fig. 1), and e is the identity operator. As shown in I, the energy (and any other expectation value of a spatial operator) can be written as

$$E = \langle G_1{}^\mu \Phi\chi | H | G_1{}^\mu \Phi\chi \rangle / \langle G_1{}^\mu \Phi\chi | G_1{}^\mu \Phi\chi \rangle ,$$
$$= \langle \Phi | H | O_{11}{}^\mu \Phi \rangle / \langle \Phi | O_{11}{}^\mu \Phi \rangle , \tag{4}$$

for any spatial function Φ and spin function χ. Thus the spin terms may be immediately eliminated and only $O_{11}{}^\mu$ of the operators in (3) is actually needed here.

In the G1 method we take the Φ and χ in (4) to be product functions,

$$\Phi(1,2,3) = \phi_{1a}(1)\phi_{1b}(2)\phi_{2a}(3) , \tag{5}$$

$$\chi(1,2,3) = \alpha(1)\beta(2)\alpha(3) , \tag{6}$$

and optimize all of the orbitals, i.e., we find the set leading to a stationary energy. The result is a set of equations (called the G1 equations) the solution of which are the optimum orbitals.

$$H^{1a}\phi_{1a} = \epsilon_{1a}\phi_{1a} ,$$
$$H^{1b}\phi_{1b} = \epsilon_{1b}\phi_{1b} , \tag{7}$$
$$H^{2a}\phi_{2a} = \epsilon_{2a}\phi_{2a} .$$

Each operator H^i in (7) can be written as

$$H^i = h + U^i , \tag{8}$$

where[10] $h = -\frac{1}{2}\nabla^2 - Z/r$ for an atom with nuclear charge Z and U^i is an average potential due to the other two electrons. Thus each optimized orbital (called a G1 orbital) is an eigenstate of an electron moving in the average potential U^i due to the other electrons (U^i involves the other $N-1$ orbitals and includes permutation operators and h). Equations (7) are solved by taking a Roothaan expansion[11] in terms of a set of basis functions $\{X_\mu\}$,

$$\phi_i = \sum_\mu X_\mu C_{\mu i} , \tag{9}$$

which leads to the following equations[12]:

$$H_{\mu\nu}{}^i C_{\nu j} = S_{\mu\nu} C_{\nu j} \epsilon_j{}^i , \quad i = 1, 2, 3 \tag{10}$$

FIG. 1. The Young tableaux for three-electron doublet states. $S_1^{[2,1]} = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array}$ $S_2^{[2,1]} = \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 \\ \cline{1-1}\end{array}$

[7] W. A. Goddard, III, Phys. Rev. **157**, 73 (1967), hereafter called I.

[8] Note that $\omega_{1\bar{1}}{}^\mu \alpha\beta\alpha$ and $\omega_{2\bar{1}}{}^\mu \alpha\beta\alpha$ are both doublet spin functions and that the combination of $O_{ij}{}^\mu$ to use in $G_1{}^\mu$ is just the one such that $G_1{}^\mu$ is antisymmetric in the *particle* (space plus spin) coordinates.

[9] D. E. Rutherford, *Substitutional Analysis* (Edinburgh University Press, London, 1948).

[10] Atomic units are used. Thus $\hbar = 1$, $e = 1$, and $\mu_e = 1$, where μ_e is the reduced electron mass. Thus the main correction for the finite mass of the nucleus is included, but the units depend on the nucleus mass. Hence the unit of energy is the reduced Hartree, $h_M = (27.210)M/(M+m_e)$ eV and the unit of length is the reduced Bohr, $a_0 = (0.52917)(M+m_e)/M$ Å. Alternatively, for comparison to molecular calculations in which the nuclei are fixed (masses assumed to be infinite), we can consider the present calculations to be in unreduced atomic units (with $m_e = 1$).

[11] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

[12] The Einstein summation convention is used for Greek subscripts.

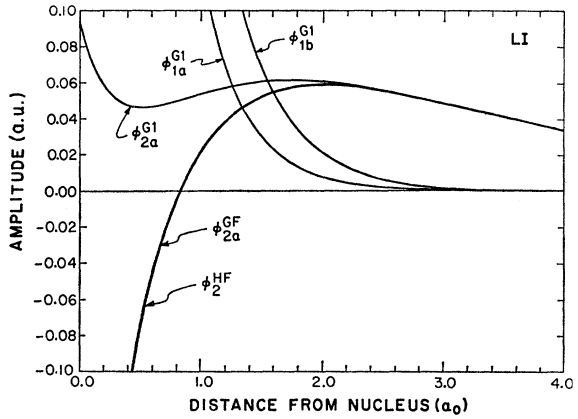

FIG. 2. The G1, GF, and HF valence orbitals for Li.

for the expansion coefficients. (The explicit forms of the H^i matrices are given in Appendix A.) Since the H^i involve the unknown coefficients, Eqs. (10) must be solved iteratively.

As shown in IV,[3] the cusp conditions and the Koopmans, Hellmann-Feynman, Brillouin, and virial theorems apply to G1 wave functions.

III. CALCULATIONS

Calculations on Li were carried out with various basis sets,[13] each using optimized orbital exponents, until a satisfactory basis set was found. The various basis sets[14] are shown in Table I with the total energy E; virial ratio, $V/2E$ (should be 1.0 for a properly scaled basis set); and cusps (the cusps should be 3.0 for all three G1 orbitals). We found that the type of basis set proposed by Roothaan and Kelly[15] (Slater orbitals $1s$, ns, $n's$, $\cdots$, $n''s$, where n, n', $\cdots$, $n'' \geqslant 3$) is necessary in order to obtain good cusps with a reasonable number of functions. Basis sets $d5$, $e6$, and $f6$ did not have the orbital exponent for the $1s$ basis functions optimized. This is clearly a restriction for $d5$, $e6$, and $f6$ since the virial ratio $V/2E$ is too far from 1.0 (generally a well-optimized calculation should have $|V/2E-1.0| \leqslant 5\times10^{-6}$). On the other hand, basis sets Li $h7$, Be^+ $i6$, and B^{++} $j6$ are complete enough so that the virial ratio and cusp conditions are simultaneously satisfied. Upon optimization of ζ_{1s} for these three sets the energy changed by less than one part in 10^8; hence the optimum value of ζ_{1s} is Z, and no restriction has been imposed.

TABLE II. Expansion coefficients for the G1 orbitals of Li, Be^+, and Be^{++}. The basis functions are in the same order as in Table I.

Li$a3$		Li$h7$		Be^+i6		$B^{++}j6$	
ϕ_{1a}	0.72125	ϕ_{1a}	1.14339	ϕ_{1a}	1.14394	ϕ_{1a}	1.14136
	0.29765		−0.10516		−0.07634		−0.02179
	0.00197		−0.07724		−0.10769		−0.16128
			0.00739		0.01241		0.02082
			0.01130		0.00318		−0.00288
			0.00813		−0.00043		0.00206
			0.00330				
ϕ_{1b}	−0.16544	ϕ_{1b}	0.61010	ϕ_{1b}	0.67069	ϕ_{1b}	0.71003
	1.15002		0.12841		0.10122		0.05852
	−0.00776		0.07783		0.11102		0.17699
			0.27126		0.18992		0.11746
			−0.00168		0.00007		−0.00099
			0.00295		0.00067		0.00047
			−0.00106				
ϕ_{2a}	0.04212	ϕ_{2a}	0.03195	ϕ_{2a}	0.05003	ϕ_{2a}	0.06097
	−0.03619		−0.00167		−0.00197		−0.00089
	1.00407		0.00065		0.00076		0.00157
			0.02044		0.02648		0.02760
			0.28904		0.38657		0.38849
			0.64649		0.62404		0.60678
			0.11219				

[13] The basis functions are Slater orbitals which have the form $\chi_{n0}(r)=Nr^{n-1}e^{-\zeta r}$, where N is a normalizing constant and ζ is called an orbital exponent. Such an orbital is referred to as an ns orbital.

[14] The orbital exponents given in Table I have generally included about one more place than were reliably optimized.

The expansion coefficients for the G1 orbitals are given in Table II for basis sets Li $a3$, Li $h7$, Be^+ $i6$, and B^{++} $j6$.

IV. DISCUSSION

A. Nodeless Orbitals

In Figs. 2 and 3 we show the G1 orbitals for Li (basis set $h7$). For comparison, the HF and GH orbitals are also shown. The most significant difference is that *none of the G1 orbitals has a node.* We see that the core orbitals ϕ_{1a} and ϕ_{1b} die off monotonically and are similar in shape to the HF or GF core orbitals. However, the G1 core orbitals are split far more than the corresponding GF orbitals [$\phi_{1a}(0)/\phi_{1b}(0)=1.87$ for the G1 case and 1.02 for the GF case]. The valence orbital for the G1 wave function is ϕ_{2a}, which is really quite similar to the HF and GF orbitals for $r>2.25a_0$ (the core extends to about $1.5a_0$). That is, the three methods lead to valence orbitals with nearly identical amplitudes in

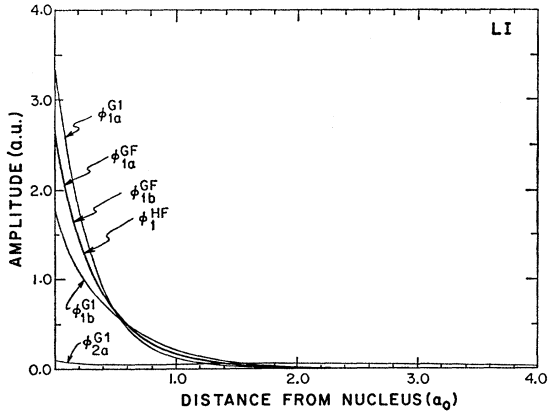

FIG. 3. The core orbitals for the G1, GF, and HF wave functions of Li.

[15] C. C. J. Roothaan and P. S. Kelly, Phys. Rev. 131, 1177 (1963).

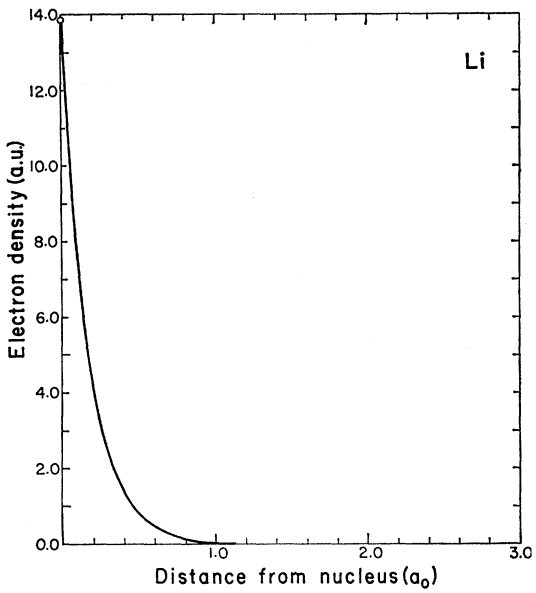

FIG. 4. The electron density of Li from G1, GF, and HF calculations.

the region where the valence orbital dominates. However, the valence G1 orbital differs drastically from the HF and GF orbitals in the core region in that the G1 valence orbital has no node.[16] The only theoretical condition on the orbitals in this region is that the cusp condition should be satisfied at the nucleus, but the valence orbitals of all three methods satisfy this condition. One might suspect that this odd behavior would lead to odd variations in, say, the density or spin density,[17] but we see from Figs. 4 and 5 that the three methods lead to nearly identical density distributions and to rather similar spin-density distributions. In addition, as discussed in Sec. IV C 1, the HF, GF, and G1 wave functions lead to essentially identical values for $\langle\sum_i r_i^2\rangle$ and orbital energy. Thus, despite the unusual shape of the G1 valence orbital, the expectation values obtained from the G1 wave function are all quite reasonable.

The significant difference here between the G1 and the HF and GF methods is that in both the HF and GF cases the form of the wave function *forces*[18] the valence orbital to be orthogonal to a core orbital, whereas no such constraint is involved in the G1 case. Of course, the G1 wave function could allow the valence orbital to be orthogonal to a core orbital and

[16] The lack of orthogonality between the valence orbital and the core orbitals does not lead to any problems, such as collapsing of the valence orbital into the core, because the many-electron wave function satisfies Pauli's principle, and it is the total energy for all the electrons which is optimized.

[17] We use the expression "spin density" to refer to the following expectation value: $Q(\mathbf{R})\equiv\langle\sum_i\delta(\mathbf{r}_i-\mathbf{R})\hat{s}_{zi}\rangle/S$ for a state of spin multiplicity $2S+1$.

[18] The GF and HF wave functions are essentially invariant under the transformation orthogonalizing the valence orbital to the core opticals.

TABLE III. Comparison of results from HF, GF, and G1 calculations on the ground state of Li. (Hartree atomic units are used.[a])

	HF[b]	GF[c]	G1
E	−7.432727	−7.432813	−7.447560
ϵ_{1a}	−2.471	−2.499	−2.843
ϵ_{1b}	−2.471	−2.464	−2.458
ϵ_{2a}	−0.1963	−0.1965	−0.1962
$\langle\sum\delta(r)\rangle$	13.82	13.83	13.86
$Q(0)$	0.167	0.241	0.210
$\langle\sum r^2\rangle$	18.63	18.59	18.65
$\phi_{1a}(0)$	2.614	2.636	3.352
$\phi_{1b}(0)$	2.614	2.594	1.788
$\phi_{2a}(0)$	−0.4074	−0.4025	0.0937

[a] See Ref. 10.
[b] Using the 12 basis function wave function of Roothaan, Sachs, and Weiss (Ref. 19).
[c] Using the eight basis function wave function of Goddard (Ref. 4).

hence have a node if such behavior would lead to lower energies. But, in fact, we see that the G1 wave function leads to far lower energies than either the GF[4] or HF[19] methods ($E_{GF}-E_{HF}=-0.000086$, $E_{G1}-E_{HF}=-0.014747$, see Table III). Thus the nodes in the HF and GF orbitals are due to a constraint in the form of the wave function and not to something physical.

In addition, from simple physical considerations we would expect for the valence orbitals to be nodeless. Consider a valence electron moving in the average potential $V=-Z/r+U$ due to the nucleus and core electrons. We would expect this total potential in the core region to be roughly uniform with a negative infinity at the origin, and for large r we expect $V\sim-1/r$.

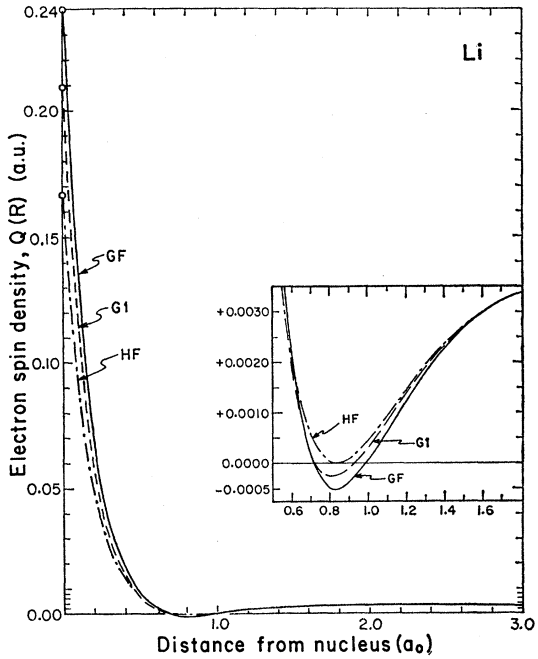

FIG. 5. The spin density $Q(R)=\langle\sum\delta(\mathbf{r}_i-\mathbf{R})\hat{s}_z(i)\rangle$ of Li from G1, GF, and HF calculations.

[19] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960).

TABLE IV. Correlation energies[a] for atoms using G1, GF,[b] and HF[c] wave functions. The energies are in reduced Hartree units[d] and the nuclear charge is Z.

Z		Number of electrons 2 $^1S_0$	3 $^2S_{\frac{1}{2}}$
1	G1	0.0139	
	GF	0.0139	
	HF	0.0398	
2	G1	0.0257	
	GF	0.0257	
	HF	0.0420	
3	G1	0.0285	0.0305
	GF	0.0285	0.0452
	HF	0.0435	0.0453
4	G1	0.0298	0.0332
	GF	0.0298	0.0472
	HF	0.0443	0.0474
5	G1		0.0349
	GF		0.0485
	HF		0.0488

[a] The "exact nonrelativistic" energies are from Scherr, Silverman, and Matsen, Phys. Rev. **127**, 830 (1962).
[b] The GF correlation energies are based on Goddard (Ref. 4).
[c] The HF correlation energies are based on Roothaan, Sachs, and Weiss (Ref. 19).
[d] See Ref. 10.

Thus we expect the valence orbital to have a cusp at the origin, a minimum in the core region, a maximum outside of the core, and an exponential drop off at large r. That is, we would expect that the lowest state for an electron moving in the potential V would be nodeless.[20] Hence the G1 orbitals for Li are certainly quite consistent with our physical expectations of what the orbitals of an independent-particle wave function should be like. The HF and GF valence orbitals, on the other hand, each have a node in the core region (due to the forced orthogonalization) and have very large amplitudes near the nucleus. Thus we conclude that the *nodes* in the valence orbitals for HF and GF wave functions for Li are purely artifacts of these methods due to nonphysical orthogonalization constraints and *have no physical significance whatsoever.*

The above results would indicate that for larger atoms nodes may occur in ground-state orbitals only when required by symmetry, as for a p or d function. This may lead to some modifications in our ideas concerning the ground and excited states of atoms. Thus each Rydberg series for Li starts with a term in which the electron is in a radially nodeless orbital with successively one more node for each term. In addition, in the calculation of band structures for solids some problems involving orthogonalization of conduction states to core states may now be ameliorated. Attempts have already been made along these lines and within the framework of the HF method through the use of pseudopotentials.[21,22] We now see that by abandoning the HF framework in favor of the G1 framework we not only eliminate the core orthogonalization conditions in an *ab initio*, direct, natural, and nonarbitrary way but in addition get much better energies.

[20] It is easy to show that the lowest state of an electron moving in a local potential is nodeless. However, this does not necessarily apply to HF, GF, or G1 orbitals since the potentials contain exchange-type terms and hence need not be local. On the other hand, the nonlocal terms are usually small enough so that the lowest orbital is nodeless.

B. Correlation

We have previously shown[4] that the HF, GF, and G1 wave functions do not contain correlation. That is, each orbital is optimum for an electron moving in the field due to the other electrons, and thus each orbital is adjusted only for the average positions of the other electrons rather than for the instantaneous positions. We compared the GF correlation energies and the HF correlation energies and found that the GF correlation energies are significantly smaller for the two- and four-electron atoms, but for three-electron atoms the GF and HF energies are nearly the same. This apparent inbalance does not occur for the G1 method. (See Table IV, where for several two- and three-electron atoms the correlation energies using G1, GF, and HF wave functions are reported.) The G1 method removes 65.2–32.7% of the HF correlation energy for H^- to Be^{++} and 32.6–28.4% for Li to B^{++}.

The increases in correlation energy for Li^+ to Li and for Be^{++} to Be^+ are 0.0020 and 0.0034 for the G1 case and 0.0018 and 0.0031 for the HF case. That is, for these systems the G1 and HF methods predict quite similar increases in correlation energy upon adding electrons. The increases in correlation energy for ions of increasing Z in the two-electron sequence (starting at H^-) are 0.0118, 0.0028, and 0.0013 for the G1 (and GF[23]) case as compared to 0.0022, 0.0015, 0.0008 for the HF case. For the three-electron sequence the differences are 0.0027 and 0.0017 for the G1 case and 0.0021 and 0.0012 for the HF case. Thus within an isoelectronic sequence the correlation energies increase much faster in the G1 case than in the HF case (this in spite of the G1 correlation energies being much smaller). That is, as compared to the HF method, the G1 method is relatively more effective for less positively charged systems. This, of course, is expected since the splitting of those orbitals which are doubly occupied in the HF wave function is due to the electron-electron repulsion[24] and should be less when this repulsion is relatively less important as compared to the other energy terms.

[21] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959); M. H. Cohen and V. Heine, *ibid.* **122**, 1821 (1961); J. M. Ziman, Advan. Phys. **13**, 89 (1964); A. U. Hazi and S. A. Rice, J. Chem. Phys. **45**, 3004 (1966).
[22] I thank Professor R. S. Berry for first bringing the pseudopotential method to my attention.
[23] For a two-electron singlet state there is one tableau, and thus the G1 and GF wave functions and energies are identical.
[24] In the absence of electron-electron interactions, the many-electron Hamiltonian is separable; hence the HF and G1 wave functions are equal to the exact wave function and thus identical. That is, the orbitals are not split.

Since the G1, GF, and HF wave functions can all be given an independent-particle interpretation and thus none of them contains instantaneous electron correlation, we could define correlation energy in terms of any of these methods. However, of the three the G1 method yields the lowest energies and hence the other methods still contain what could be called a static (nondynamic or noninstantaneous) correlation error. In addition, the G1 method seems to treat systems with different numbers of electrons in a comparable way. Thus it would seem that correlation should be defined with respect to the G1 wave function. That is, the difference between the exact energy and the G1 energy is essentially the energy error due to dynamic or instantaneous correlation among the electrons.

In the ground states of two- and three-electron atoms the HF, GF, and G1 orbitals are all s orbitals. Thus for these methods the many-electron wave functions contain no angular correlations between electrons and are referred to as (many-electron) radial wave functions. The best possible radial wave function [including configuration interaction (CI)] is called the radial limit. For the two-electron atoms (H^-, He, Li^+, Be^{++}) we have already seen[4] that the G1 (and GF) wave functions are nearly at the radial limit ($E^{G1}-E^{RL}=0.001$ for He). The same situation seems to occur in the three-electron case, where for Li the G1 energy is -7.447560 which is far better than the best published values (-7.4420 by Weiss[25] and -7.4422 by Brown and Fontana[26]) of which we are aware for radial configuration interaction wave functions. Since even for three basis functions the G1 energy (-7.446137) is much better than these CI values, it seems reasonable to presume that the G1 energy is nearly at the radial limit (probably about 0.001 to 0.002 off).

Thus essentially all additional improvements in the wave function beyond the G1 result must be due to angular correlations since there are almost no dynamic radial correlations left to account for. This leads to the following physical picture from the G1 wave function of Li: Of the two-core electrons, one is at the inner part of the core while the other is at the outer part, thus allowing a static (nondynamic) correlation of these electrons since they are in different regions. The valence electron is then outside this core region. When these regions (all of which overlap) are optimally adjusted, we obtain a description which almost completely eliminates the necessity of further instantaneous radial correlations among these electrons. This wave function errs in that it lacks angular correlations among the electrons. Such angular correlation allows electrons at the same r to slip around on different sides of the nucleus and thus keeps the repulsion energy to a minimum while decreasing the distance of the electrons from the nucleus. Thus the G1 wave functions and other wave functions near the radial limit are generally more expanded than the exact wave functions.

Next we will consider several other types of wave functions and compare them to the G1 wave functions.

C. Comparison with Other Wave Functions

We will first compare the various methods (HF, GF, and G1) leading to independent-particle wave functions.

1. *Comparison of HF, GF, and G1 Methods*

The GF wave function for Li is

$$G_f{}^{\mu}[\phi_{1a}'(1)\phi_{2a}'(2)\phi_{1b}'(3)\alpha(1)\alpha(2)\beta(3)], \tag{11}$$

where

$$G_f{}^{\mu}=O_{22}{}^{\mu}\omega_{\bar{2}\bar{2}}{}^{\mu}-O_{12}{}^{\mu}\omega_{\bar{1}\bar{2}}{}^{\mu}, \tag{12}$$

$$\begin{aligned}
O_{22}{}^{\mu}&=\tfrac{1}{6}[2e-(123)-(132)-2(12)+13)+(23)],\\
O_{12}{}^{\mu}&=\tfrac{1}{6}\sqrt{3}[(123)-(132)-(13)+(23)],\\
\omega_{\bar{2}\bar{2}}{}^{\mu}&=\tfrac{1}{6}[2e-(123)-(132)+2(12)-(13)-(23)],\\
\omega_{\bar{1}\bar{2}}{}^{\mu}&=\tfrac{1}{6}\sqrt{3}[-(123)+(132)-(13)+(23)];
\end{aligned} \tag{13}$$

and the HF wave function is[27]

$$\mathcal{A}[\phi_1(1)\phi_1(2)\phi_2(3)\alpha(1)\beta(2)\alpha(3)]. \tag{14}$$

We have already shown in II that

$$\begin{aligned}
c_1G_1{}^{\mu}(\phi_1\phi_1\phi_2\alpha\beta\alpha)&=c_2G_f{}^{\mu}(\phi_1\phi_2\phi_1\alpha\alpha\beta)\\
&=\mathcal{A}(\phi_1\phi_1\phi_2\alpha\beta\alpha),
\end{aligned} \tag{15}$$

where c_1 and c_2 are constants. Thus the HF wave function is a special case of both the G1 and GF wave functions, and hence the G1 and GF methods in general lead to energies better than the HF energy. We have also noted in II that a function of the form $\mathcal{A}(\phi_{1a}\phi_{1b}\phi_{2a}\alpha\beta\alpha)$ is *not* an eigenfunction of $\hat{S}^2$ if $\phi_{1a}\neq\phi_{1b}$ and that the doublet spin projection of this function is just $G_f{}^{\mu}(\phi_{1a}\phi_{2a}\phi_{1b}\alpha\alpha\beta)$. That is, the natural generalization of the HF method in which we allow all orbitals to be different, in which we spin-project to obtain an eigenfunction of $\hat{S}^2$, and in which we *then* optimize all the orbitals corresponds to the GF method (also called the spin-polarized extended HF method).

The G1 wave function is quite different from this and cannot be written as a spin-projected Slater determinant. In Sec. IV C3 we show that the G1 wave function corresponds to a natural generalization of the valence-bond method. In the case of Li the G1 wave function may be expanded as[27]

$$\begin{aligned}
&G_1(\phi_{1a}\phi_{1b}\phi_{2a}\alpha\beta\alpha)\\
&\quad=\tfrac{2}{3}[\mathcal{A}(\phi_{1a}\phi_{1b}\phi_{2a}\alpha\beta\alpha)+\mathcal{A}(\phi_{1b}\phi_{1a}\phi_{2a}\alpha\beta\alpha)]\\
&\quad=\tfrac{2}{3}\mathcal{A}[(\phi_{1a}\phi_{1b}+\phi_{1b}\phi_{1a})\phi_{2a}\alpha\beta\alpha],
\end{aligned} \tag{16}$$

[25] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

[26] R. T. Brown and P. R. Fontana, J. Chem. Phys. **45**, 4248 (1966).

[27] $\mathcal{A}=(1/N!)\sum_{\tau}\zeta_{\tau}\tau$ is the antisymmetrizer, where ζ_{τ} is the parity of the permutation τ.

and the GF wave function may be expanded as

$$G_f(\phi_{1a}\phi_{2a}\phi_{1b}\alpha\alpha\beta) = \tfrac{4}{3}[\mathcal{A}(\phi_{1a}\phi_{2a}\phi_{1b}\alpha\alpha\beta)+\tfrac{1}{2}\mathcal{A}(\phi_{1b}\phi_{2a}\phi_{1a}\alpha\alpha\beta) +\tfrac{1}{2}\mathcal{A}(\phi_{1a}\phi_{1b}\phi_{2a}\alpha\alpha\beta)], \quad (17)$$

which demonstrates the differences between G_1 and G_f and the similar limit for $\phi_{1a}=\phi_{1b}$.

The G1 method leads to far better energies for Li than either the HF or the GF methods but we see in Table III that ϵ_{2a} (by Koopmans's theorem approximately the negative of the first ionization energy) is quite similar for all three as are the expectation values of the spatial operators $\sum_i \delta(\mathbf{r}_i)$ (the density of electrons at the nucleus) and $\sum_i r_i^2$ and indeed the entire density maps (see Fig. 4). For spin density[17] near the nucleus the three methods differ significantly, but all three lead to nodes or near nodes near $0.85a_0$ and similar spin densities for larger r (see Fig. 5).

Thus on the basis of predicted physical properties, the three methods are rather similar except that the G1 method leads to much better energies than the other two and the HF method has somewhat poorer spin densities at the nucleus.

Wave functions of the G1 form [Eqs. (1) or (16)] have also been calculated for Li by Hurst *et al.*[28] ($E=-7.4436$) and by Ritter *et al.*[29] ($E=-7.4450$). These calculations used three- and six-basis functions, respectively, but did not optimize the orbitals self-consistently. From Table I we see that for three basis functions the energy is -7.4461, if calculated self-consistently, while it is -7.4476 if large basis sets are used. Of course, if the calculations are not done self-consistently, we do not obtain an independent-particle interpretation.

We next compare the G1 wave function to some electron-pair-type wave functions.

2. *Paired-Type Wave Functions*

In Appendix D we show that

$$G_1{}^{\gamma}\Phi\chi = c_1\mathcal{A}[(N_1P_1\Phi)\chi] = c_2\mathcal{A}[(P_1\Phi)\chi] \quad (18)$$

for any spatial function Φ, where P_1 (the row symmetrizer) and N_1 (the column antisymmetrizer) are defined in Appendix C and $\chi=\alpha(1)\beta(2)\alpha(3)\beta(4)\cdots$ as given in (D3). For a three-electron doublet, $P_1=[e+(12)]$ and $N_1=[e-(13)]$. The function

$$\mathcal{A}[(P_1\Phi)\chi] \quad (19)$$

is of the form suggested by Hurley, Lennard-Jones, and Pople[30] in 1953. The only difference is that they assumed a singlet state, wrote

$$P_1\Phi(1\cdots N) = \Theta_1(1,2)\Theta_2(3,4)\cdots, \quad (20)$$

and then required that

$$\int \Theta_i(1,2)\Theta_j(1,2)d\mathbf{x}_1 = 0 \quad \text{if} \quad i\neq j. \quad (21)$$

This latter condition, known as strong orthogonality (SO), is a constraint on the wave function. The function (19) with (20) and strong orthogonality is usually called a separated-pairs wave function.[31] The function $\mathcal{A}[(N_1P_1\Phi)\chi]$ of (18) is of the form suggested by Matsen.[32]

If Φ is taken to be a product of one-electron orbitals, then

$$\mathcal{A}[(P\Phi)\chi] = \mathcal{A}[(\phi_1\phi_2+\phi_2\phi_1)(\phi_3\phi_4+\phi_4\phi_3)\cdots\alpha\beta\alpha\beta\cdots],$$

and thus all three expressions in (18) have the form of a generalized valence bond wave function. That is, the G1 method corresponds to a generalization of the valence bond method in which all the orbitals are completely optimized (instead of being restricted to be atomic orbitals), in which the core orbitals are not forced to be identical in pairs, and in which no *ad hoc* orthogonalization conditions are assumed between orbitals.

For all three wave functions in (18), the expression for the energy after summing over the spin coordinates is

$$E = \langle\Phi|H|O_{11}\Phi\rangle/\langle\Phi|O_{11}\Phi\rangle.$$

That is, an advantage of the $G1$ operator is that it allows the spin terms to be immediately eliminated.

Wave functions of the form $\mathcal{A}[(P\Phi)\chi]$ with a product Φ and with the SO constraint have been called extended valence bond (EVB) wave functions by Slater[33] and paired-electron orbital functions by Hurley, Lennard-Jones, and Pople.[30] The proper optimization of the orbitals for such a function would be quite complex due to the number of off-diagonal Lagrange multipliers needed to ensure SO. However, Slater has constructed approximate EVB orbitals from virtual and occupied HF orbitals,[33] and Klessinger and McWeeny[34] have approximately optimized the orbitals for several systems by arbitrarily partitioning orthogonal basis functions among the orbital pairs.

The nonbonding and inner shell orbitals have been taken as doubly occupied in the EVB method. However, this means that for atoms the EVB wave functions are identical to HF wave functions. Consequently, in discussing the EVB method in this paper we will allow

[28] R. P. Hurst, J. D. Gray, G. H. Brigman, and F. A. Matsen, Mol. Phys. **1**, 189 (1958).
[29] Z. W. Ritter, R. Pauncz, and K. Appel, J. Chem. Phys. **35**, 571 (1961).
[30] A. C. Hurley, J. Lennard-Jones, and J. A. Pople, Proc. Roy. Soc. (London) **A220**, 446 (1953).
[31] J. M. Parks and R. G. Parr, J. Chem. Phys. **28**, 335 (1958).
[32] F. A. Matsen, Advan. Quantum Chem. **1**, 59 (1964).
[33] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1963), Vol. 1, p. 196.
[34] M. Klessinger and R. McWeeny, J. Chem. Phys. **42**, 3343 (1965); M. Klessinger, *ibid.* **43**, S117 (Z965).

even the inner shell EVB orbitals to split. Next we will consider the effect of the strong orthogonality constraint.

3. *Effect of Strong Orthogonality*

The G1 valence orbital (ϕ_{2a}) is not at all orthogonal to the core orbitals (the overlaps for Li are 0.14 and 0.23, see Table V). In order to determine how sensitive the wave function is to this overlap and to test the effect of SO, the G1 valence orbital was orthogonalized to the core orbitals (see Table VI). This caused the energy to increase by over 7 eV, yielding an energy worse than the HF and GF energies. Of course, we did not optimize the orbitals under the SO constraint (which would yield the EVB wave function), and if we had the energy would surely be better than the HF energy (since the HF orbitals are also strongly orthogonal). The strongly orthogonal 2a orbital is binodal, which explains the high energy obtained here. This binodal character results because the $\phi_{1a}{}^{G1}$ and $\phi_{1b}{}^{G1}$ orbitals are concentrated in such different radial regions. Thus it appears that in the EVB case the optimum core orbitals would be only slightly split in order to avoid extra conditions on $\phi_{2a}{}^{EVB}$. In this case the EVB energy and orbitals would be similar to (but not identical with) the GF orbitals.

An approximate relationship between GF energies and EVB energies is plausible. The GF orbitals can be transformed in such a way that the new orbitals form strongly orthogonal pairs but with the energy and all expectation values unchanged (this is the transformation diagonalizing the matrix $S_{ij}=\langle\phi_{ia}|\phi_{jb}\rangle$). Thus the GF orbitals can be considered as the optimum strongly orthogonal orbitals for a $G_f\Phi_\chi$ type wave function. Also for identical core orbitals ($\phi_{1a}=\phi_{1b}=\phi_1$) the HF, GF, G1, and EVB type wave functions are all the same [from (15) and (18)]. But we already know that the GF orbitals of Li are only slightly split ($\langle\phi_{1a}|\phi_{1b}\rangle=0.99989$), and we have evidence above that the EVB core orbitals must be split much less than the G1 orbitals. Thus, if the EVB orbitals are only slightly split, the EVB, GF, and HF wave functions should all lead to quite similar energies. Although the GF wave function with the SO orbitals is not identical to the EVB wave function with the same strongly orthogonal orbitals, it does have a similar energy (the GF energy for Li is -7.432813, the energy of the EVB wave function using the transformed GF orbitals is -7.432753).

Strong orthogonality in the EVB wave function leads to a node in the valence orbital and gives rise to energies near the HF and GF energies, both of which also have nodes in the valence orbital. The fact that all of these methods forcing nodes in the valence orbital lead to much worse energies than the G1 energy is another argument for the importance of the nodeless character of the valence orbital.

TABLE V. Orbital overlaps for the G1, GF, and HF orbitals of Li.

	$\langle\phi_{1a}\|\phi_{1b}\rangle$	$\langle\phi_{1a}\|\phi_{2a}\rangle$	$\langle\phi_{1b}\|\phi_{2a}\rangle$
HF	1.0	0.0	0.0
GF[a]	0.99989	0.0	0.00369
G1[b]	0.92822	0.14005	0.23309

[a] Goddard (Ref. 4). [b] Basis set *h*7.

Because of SO, the paired functions in separated paired and EVB wave functions cannot contribute to the spin density. Thus for atomic states such as Li ^2P, N ^4S, Mn^{++} ^6S, C ^3P, O ^3P, etc., these methods will predict zero spin density at the nucleus and hence no Fermi contact contribution to the hyperfine splitting. This, of course, is a well-known defect of the HF method. (A similar problem arises for spin densities at nuclei in the plane of molecules having only unpaired π electrons.) Similarly, for a system such as Li ^2S, the separated-pair-type wave function leads to a $Q(0)$[17] of $|\phi_{2a}(0)|^2$, i.e., just the same as for the HF case. For wave functions without SO the spin density can involve all pairs, but even so the $Q(0)$ for the G1 wave function of Li ^2S is 9% off. For a state such as Li ^2P, where the core electrons are by symmetry orthogonal to the unpaired electrons, then the G1 wave functions leads to zero $Q(0)$ just as do SO wave functions.

V. SUMMARY

The G1 wave function for Li leads to much better energies than does the HF and GF wave functions, yet the G1 method retains the independent-particle interpretation. Thus, since the G1 wave function does not contain dynamic or instantaneous correlation between the electrons, we could reasonably define correlation energy with respect to the G1 energy rather than with respect to the HF energy.

Just as for the two-electron atoms the G1 wave functions for three-electron atoms are nearly at the radial limit. That is, for these systems the dynamic correlation energy is essentially all due to angular correlations; dynamic radial correlation is only very slight.

The density distributions obtained from the HF, GF, and G1 wave functions are nearly identical, but the errors in the spin density at the nucleus for the three methods are 28, 4, and 9%, respectively. Despite the

TABLE VI. The effect of strong orthogonality upon the G1 wave function (basis set *h*7). (Hartree atomic units are used.[a])

	Strong orthogonality	No restriction
E	-7.180038	-7.447560
$V/2E$	1.037773	1.000001
$\langle\sum\delta(r_i)\rangle$	14.144	13.864
$Q(0)$	0.4109	0.2095
$\langle\sum r_i^2\rangle$	19.512	18.654
$\phi_{2a}(0)$	0.6410	0.09366

[a] See Ref. 10.

large difference in shape between the G1 and the HF and GF valence orbitals, all three lead to essentially the same orbital energy.

In contrast to the HF and GF methods, the G1 method does not force orthogonality between valence electrons and core electrons. The G1 wave function would allow such orthogonality if it were energetically favorable, but in fact we find that the resulting valence orbitals have significant overlaps with the core orbitals resulting in a significant decrease in the energy. The resulting G1 valence orbitals are nodeless with a form quite like that expected on physical grounds (cusp at the origin, minimum in the core region, maximum outside the core, and exponential falloff far outside the core). This is in contrast to the HF and GF valence orbitals which have nodes. We conclude that such nodes are artifacts related to unphysical constraints built into the wave function. The lack of orthogonality conditions between valence orbitals and core orbitals for G1 wave functions may remove problems due to this orthogonality in considering bands of states in solids and Rydberg series in molecules and atoms.

The G1 wave function has the form of a paired electron wave function. Thus the extended valence bond wave function is a special case of the G1 wave function in which a constraint, SO, is assumed. Since SO has a quite deleterious effect on G1 wave functions for Li, we conclude that SO is an inappropriate constraint for orbital-type wave functions. As a result, we suggest that for Li the EVB method should yield energies similar to the GF energy and much worse than the G1 energy.

APPENDIX A

The explicit expressions for the G1 matrix Hamiltonians are given below. $H_{\mu\nu}^{1b}$ is obtained from $H_{\mu\nu}^{1a}$ by interchanging $1a$ and $1b$. Basis functions are indicated by μ and ν; ϕ_{1a}, ϕ_{1b}, and ϕ_{2a} are denoted by a, b, and c, respectively.

$$\begin{aligned}H_{\mu\nu}^{1a}=&\langle\mu|h|\nu\rangle D_{1a}^{1a}+\langle\mu|h|b\rangle[\langle b|\nu\rangle-\tfrac{1}{2}\langle b|c\rangle\langle c|\nu\rangle]-\tfrac{1}{2}\langle\mu|h|c\rangle[\langle c|\nu\rangle+\langle c|b\rangle\langle b|\nu\rangle]+[\langle\mu|b\rangle-\tfrac{1}{2}\langle\mu|c\rangle\langle c|b\rangle]\langle b|h|\nu\rangle\\&-\tfrac{1}{2}[\langle\mu|c\rangle+\langle\mu|b\rangle\langle b|c\rangle]\langle c|h|\nu\rangle-\tfrac{1}{2}\langle\mu|c\rangle\langle c|\nu\rangle(\langle b|h|b\rangle-E)-\tfrac{1}{2}\langle\mu|b\rangle\langle c|\nu\rangle(\langle b|h|c\rangle-E\langle b|c\rangle)\\&+\langle\mu|b\rangle\langle b|\nu\rangle(\langle c|h|c\rangle-E)-\tfrac{1}{2}\langle\mu|c\rangle\langle b|\nu\rangle(\langle c|h|b\rangle-E\langle c|b\rangle)+(\mu\nu|cc)+(\mu\nu|bb)-\tfrac{1}{2}(\mu c|c\nu)+(\mu b|b\nu)\\&-(\mu\nu|bc)\langle b|c\rangle-\tfrac{1}{2}(\mu b|c\nu)\langle b|c\rangle-\tfrac{1}{2}(\mu c|b\nu)\langle b|c\rangle+\langle\mu|b\rangle[(\nu b|cc)-\tfrac{1}{2}(\nu c|bc)]-\tfrac{1}{2}\langle\mu|c\rangle[(\nu c|bb)+(\nu b|bc)]\\&+\langle\nu|b\rangle[(\mu b|cc)-\tfrac{1}{2}(\mu c|bc)-\tfrac{1}{2}\langle\nu|c\rangle[(\mu c|bb)+(\mu b|bc)],\end{aligned}$$

$$\begin{aligned}H_{\mu\nu}^{2a}=&\langle\mu|h|\nu\rangle D_{2a}^{2a}-\tfrac{1}{2}[\langle\mu|h|a\rangle\langle a|\nu\rangle+\langle\mu|h|b\rangle\langle b|\nu\rangle]-\tfrac{1}{2}[\langle\mu|a\rangle\langle a|h|\nu\rangle+\langle\mu|b\rangle\langle b|h|\nu\rangle]-\tfrac{1}{2}\langle\mu|a\rangle\langle a|\nu\rangle(\langle b|h|b\rangle-E)\\&-\tfrac{1}{2}\langle\mu|b\rangle\langle b|\nu\rangle(\langle a|h|a\rangle-E)-\tfrac{1}{2}\langle\mu|a\rangle\langle b|\nu\rangle(\langle a|h|b\rangle-E\langle a|b\rangle)-\tfrac{1}{2}\langle\mu|b\rangle\langle a|\nu\rangle(\langle b|h|a\rangle-E\langle b|a\rangle)\\&-\tfrac{1}{2}[\langle\mu|h|a\rangle\langle a|b\rangle\langle b|\nu\rangle+\langle\mu|h|b\rangle\langle b|a\rangle\langle a|\nu\rangle+\langle\mu|b\rangle\langle b|a\rangle\langle a|h|\nu\rangle+\langle\mu|a\rangle\langle a|b\rangle\langle b|h|\nu\rangle]+(\mu\nu|aa)\\&+2(\mu\nu|ab)\langle a|b\rangle+(\mu\nu|bb)-\tfrac{1}{2}[(\mu b|b\nu)+(\mu a|b\nu)\langle a|b\rangle+(\mu a|a\nu)+(\mu b|a\nu)\langle a|b\rangle]-\tfrac{1}{2}\langle\mu|a\rangle[(\nu a|bb)+(\nu b|ab)]\\&-\tfrac{1}{2}\langle\mu|b\rangle[(\nu b|aa)+(\nu a|ab)]-\tfrac{1}{2}\langle\nu|a\rangle[(\mu a|bb)+(\mu b|ab)]-\tfrac{1}{2}\langle\nu|b\rangle[(\mu b|aa)+(\mu a|ab)].\end{aligned}$$

APPENDIX B

The expressions used for expectation values of one-electron properties for G1 wave functions are discussed next.

Consider a one-electron operator $F=\sum_i f(i)$, where the $f(i)$ are functions only of spatial coordinates. Then

$$\begin{aligned}\langle F\rangle&=\langle\Phi|F|O_{11}\Phi\rangle/\langle\Phi|O_{11}\Phi\rangle,\\&=\sum_{i,j}\langle\phi_i|f|\phi_j\rangle D_i^j/D,\end{aligned}\tag{B1}$$

where

$$\begin{aligned}D_{1a}^{1a}&=1-\tfrac{1}{2}|\langle 1b|2a\rangle|^2,\\D_{1a}^{1b}&=\langle 1a|1b\rangle-\tfrac{1}{2}\langle 1a|2a\rangle\langle 2a|1b\rangle,\\D_{1b}^{1b}&=1-\tfrac{1}{2}|\langle 1a|2a\rangle|^2,\\D_{2a}^{1a}&=-\tfrac{1}{2}[\langle 2a|1a\rangle+\langle 2a|1b\rangle\langle 1b|1a\rangle],\\D_{2a}^{1b}&=-\tfrac{1}{2}[\langle 2a|1b\rangle+\langle 2a|1a\rangle\langle 1a|1b\rangle],\\D_{2a}^{2a}&=1+|\langle 1a|1b\rangle|^2,\\D&=1+\langle 1a|1b\rangle^2-\tfrac{1}{2}[|\langle 1a|2a\rangle|^2+|\langle 1b|2a\rangle|^2\\&\quad+\mathrm{Re}(\langle 1a|2a\rangle\langle 2a|1b\rangle\langle 1b|1a\rangle)].\end{aligned}\tag{B2}$$

Now consider a one-electron operator $M=\sum_i m(i)\times s_z(i)$, where $m(i)$ is a spatial function. Then, using (D5),

$$\begin{aligned}\frac{1}{S}\langle M\rangle&=\langle P_1\Phi|\sum_{i_1}m(i_1)-\sum_{i_2}m(i_2)|N_2P_1\Phi\rangle/(2^{m+1}SD),\\&=\langle F\rangle-D^{-1}\{\langle a|m|a\rangle[1-|\langle b|c\rangle|^2]\\&\quad+\langle b|m|b\rangle[1-|\langle a|c\rangle|^2]\\&\quad+2\,\mathrm{Re}(\langle a|m|b\rangle[\langle b|a\rangle-\langle b|c\rangle\langle c|a\rangle])\},\\&=(2D)^{-1}\{\langle a|m|a\rangle|\langle b|c\rangle|^2+\langle b|m|b\rangle|\langle a|c\rangle|^2\\&\quad+2\,\mathrm{Re}(\langle a|m|b\rangle\langle b|c\rangle\langle c|a\rangle)\\&\quad+2\langle c|m|c\rangle(1+|\langle a|b\rangle|^2\\&\quad-2\,\mathrm{Re}[\langle a|m|c\rangle(\langle c|a\rangle+\langle c|b\rangle\langle b|a\rangle)]\\&\quad-2\,\mathrm{Re}[\langle b|m|c\rangle(\langle c|b\rangle+\langle c|a\rangle\langle a|b\rangle)]\},\end{aligned}\tag{B3}$$

where i_1 refers to the first column and i_2 to the second column of the tableau, and $\langle F\rangle$ is the expectation value

of $\sum_i m(i)$. In (B3), ϕ_{1a}, ϕ_{1b}, and ϕ_{2a} are denoted by a, b, and c, respectively.

APPENDIX C

We will now derive a useful form for the O_{11} operator.

Consider the Young tableau $S_1{}^\alpha$ of $\alpha=[2^m,1^{n-m}]$ as in Fig. 6. Let $\mathcal{P}$ be the product of the positive symmetric groups[9] of the rows of $S_1{}^\alpha$ [i.e., $\mathcal{P}=\{e,(12),(34),(12)(34),\cdots\}$] and let $\mathfrak{N}$ be the product of the negative symmetric groups of the columns of $S_1{}^\alpha$ [i.e., $\mathfrak{N}=\{e,-(13),-(15),-(35),(135),(153),\cdots,-(24),+(13)\times(24),\cdots\}$]. Now let $P_1{}^\alpha$ be the sum of all elements of $\mathcal{P}$ and $N_1{}^\alpha$ be the sum of all elements of $\mathfrak{N}$. Then

$$P_1{}^\alpha=[e+(12)][e+(34)]\cdots[e+(2m-1,2m)]$$

and

$$N_1{}^\alpha=[e-(13)-(15)-(35)+(135)+(153)\cdots]\times[e-(24)-(26)-(46)+(246)+(264)+\cdots],$$

where m is the length of the second column of $S_1{}^\alpha$ ($m=N-n$). We wish to show that

$$O_{11}{}^\alpha=(1/2^m\theta^\alpha)P_1{}^\alpha N_1{}^\alpha P_1{}^\alpha, \tag{C1}$$

where $\theta^\alpha=N!/f^\alpha$ and f^α is the degree of the α irreducible representation of the symmetric group $\mathcal{S}_N$.

Any sum of permutations can be expanded in terms of the $O_{rs}{}^\beta$; thus we may take

$$P_1{}^\alpha N_1{}^\alpha P_1{}^\alpha=\sum_{\beta rs}\lambda_{rs}{}^\beta O_{rs}{}^\beta. \tag{C2}$$

Let $O_{rr}{}^\beta$ and $O_{ss}{}^\beta$ operate on the left and right, respectively, of (C2). Then since

$$O_{rs}{}^\alpha O_{tu}{}^\beta=\delta^{\alpha\beta}\delta_{st}O_{ru}{}^\alpha, \tag{C3}$$

we obtain

$$O_{rs}{}^\beta\lambda_{rs}{}^\beta=O_{rr}{}^\beta P_1{}^\alpha N_1{}^\alpha P_1{}^\alpha O_{ss}{}^\beta, \tag{C4}$$

but from p. 29 of Ref. 9

$$O_{rr}{}^\alpha=\frac{1}{\theta}O_{rr}{}^\alpha E_{rr}{}^\alpha O_{rr}{}^\alpha, \tag{C5}$$

where E_{rr}, the Young projection operator, is given by

$$E_{rr}{}^\alpha=P_r{}^\alpha N_r{}^\alpha. \tag{C6}$$

Expanding (C4), we obtain

$$\theta O_{rs}{}^\beta\lambda_{rs}{}^\beta=O_{rr}{}^\beta P_r{}^\beta N_r{}^\beta O_{rr}{}^\beta P_1{}^\alpha N_1{}^\alpha P_1{}^\alpha O_{ss}{}^\beta.$$

But $P_r{}^\beta N_r{}^\beta O_{rr}{}^\beta P_1{}^\alpha N_1{}^\alpha=0$ if $\beta\neq\alpha$, since otherwise two elements in the same row of $S_1{}^\alpha$ are in the same column of $S_r{}^\beta$ or two elements in the same column of $S_1{}^\alpha$ are in the same row of $S_r{}^\beta$ (see pp. 14 and 21 of Ref. 9). Thus (C2) becomes

$$P_1{}^\alpha N_1{}^\alpha P_1{}^\alpha=\sum_{r,s}\lambda_{rs}{}^\alpha O_{rs}{}^\alpha. \tag{C7}$$

Now operate from the left with (1 2). The left side is invariant since $(1\ 2)P_1{}^\alpha=P_1{}^\alpha$, but on the right side we have terms with $(1\ 2)O_{rs}{}^\alpha$. In addition, for all r and s, 1 and 2 are either in the same row or the same column. Thus

$$(1\ 2)O_{rs}{}^\alpha=+O_{rs}{}^\alpha \quad 1 \text{ and } 2 \text{ in same row},$$
$$=-O_{rs}{}^\alpha \quad 1 \text{ and } 2 \text{ in second column}.$$

Hence the r and s in (C7) can be restricted to those with 1 and 2 in the same row. Similarly, we operate with (3 4) on (C7). Since 1 and 2 are in the same row, then 3 and 4 are either in the same row or in the same column, and just as above we find that the r and s in (C7) can be restricted to those with 3 and 4 in the same row. Continuing we find that $r=s=1$ is the only allowed tableau in (C7):

$$P_1{}^\alpha N_1{}^\alpha P_1{}^\alpha=\lambda_{11}{}^\alpha O_{11}{}^\alpha.$$

The constant $\lambda_{11}{}^\alpha$ is easily obtained by comparing the coefficient of e on each side of the equation. The coefficient of e in $P_1{}^\alpha N_1{}^\alpha P_1{}^\alpha$ = the coefficient of e in $P_1{}^\alpha P_1{}^\alpha N_1{}^\alpha$ (see p. 19 of Ref. 9) $=2^m$. The coefficient of e in $O_{11}{}^\alpha$ is just $1/\theta$, since $U_{11e}{}^\alpha=1$. Thus $\lambda_{11}{}^\alpha=\theta 2^m$, i.e., we obtain (C1).

In the same way we can also show that

$$N_f{}^\alpha P_f{}^\alpha N_f{}^\alpha=n!m!\theta^\alpha O_{ff}{}^\alpha, \tag{C8}$$

where $S_f{}^\alpha$ is the final standard tableau of the α shape. The only differences are that all P's are replaced by N's and vice versa, and after obtaining the expression analogous to (C7), we operate with (1 2), (2 3), (3 4), $\cdots$, $(n-1,n)$ is succession to eliminate all r and s except $r=s=f$.

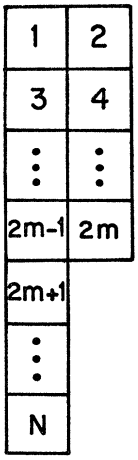

FIG. 6. The $S_1{}^\alpha$ Young tableau.

APPENDIX D

In Appendix C we showed that

$$O_{11}{}^\alpha=(1/2^m\theta)P_1{}^\alpha N_1{}^\alpha P_1{}^\alpha, \tag{D1}$$

and in Appendix C of I we showed that

$$G_1{}^\alpha\Phi\chi=f^\alpha\mathcal{A}[(O_{11}{}^\alpha\Phi)\chi]. \tag{D2}$$

(Note that $f^{\alpha}\theta^{\alpha}=N!$.) Thus

$$G_1{}^{\alpha}\Phi\chi=(f/2^m\theta)\mathcal{A}[(P_1N_1P_1\Phi)\chi].$$

But

$$\chi=\alpha(1)\beta(2)\alpha(3)\beta(4)\cdots\alpha(2m-1)\beta(2m)\times\alpha(2m+1)\cdots\alpha(N), \quad \text{(D3)}$$

and thus $\nu\chi=\chi$ for any $\nu\epsilon\mathfrak{N}$.

Hence

$$\mathcal{A}\Psi\chi=\zeta_\nu\mathcal{A}[(\nu\Psi)(\nu\chi)]=\zeta_\nu\mathcal{A}[(\nu\Psi)\chi]$$

for any spatial function Ψ, and thus

$$\mathcal{A}(N_1\Psi)\chi=n!m!\mathcal{A}(\Psi\chi). \quad \text{(D4)}$$

Hence $\mathcal{A}[(N_1P_1N_1P_1\Phi)\chi]=n!m!\mathcal{A}[(P_1N_1P_1\Phi)\chi]$. But from p. 19 of Ref. 9 $N_1P_1N_1P_1=\theta N_1P_1$; thus

$$n!m!\mathcal{A}[(P_1N_1P_1\Phi)\chi]=\theta\mathcal{A}[(N_1P_1\Phi)\chi].$$

Similarly, using (D4), we have

$$\mathcal{A}[(N_1P_1\Phi)\chi]=n!m!\mathcal{A}[(P_1\Phi)\chi];$$

thus

$$G_1{}^{\alpha}\Phi\chi=(f/n!m!2^m)\mathcal{A}[(N_1P_1\Phi)\chi]=(f/2^m)\mathcal{A}[(P_1\Phi)\chi]. \quad \text{(D5)}$$

This expression is used in the discussion of paired-type wave functions.

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Intra-Atomic Magnetic Interactions for f Electrons*

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An examination is made of the effects of spin-spin and spin–other-orbit interactions on the energy levels of f-electron configurations. The theory is applied to several rare-earth atoms and ions under a number of simplifying assumptions. Considerable improvements in the fits between experiment and theory are obtained, particularly for the sextets of Gd IV. Electrostatically correlated spin-orbit interaction is studied and found not to be susceptible to parametric absorption into the ordinary spin-orbit and spin–other-orbit interactions. The various contributions to the effective Hamiltonian for two electrons are decomposed into parts having well-defined group-theoretical properties, in preparation for their calculation for any configuration f^N.

I. INTRODUCTION

TERM analyses of complex atomic configurations are usually performed with a Hamiltonian comprising two parts: the Coulomb interaction between the electrons and the spin-orbit coupling. The procedure introduces as parameters certain Slater integrals (such as the F^k, or, equivalently, the linear combinations E^k of Racah[1]), and a few spin-orbit coupling constants ζ_l.[2] In recent years, most efforts at improvement have been centered on the study of configuration interaction. This has as its origin the large off-diagonal matrix elements of the Coulomb interaction. Its effect can be accommodated by introducing effective operators that act only within the configuration under study. The additional parameters that enter in the lowest order of perturbation theory are associated with two-electron operators (the parameters α and β of Trees[3] fall in this class) or with three-electron operators.[4] Under these limitations, the total number of parameters necessary to describe a configuration f^N is 14 [corresponding to ζ_f, $F^k(k=0, 2, 4, 6)$, α, β, γ, and six parameters T^k for the three-electron operators].

A parametrization of such a kind neglects the contributions to the Hamiltonian coming from the Breit operator H_B, given by [5]

$$H_B=-\tfrac{1}{2}e^2\sum_{i>j}[(\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j)r_{ij}^{-1}+(\boldsymbol{\alpha}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\alpha}_j\cdot\mathbf{r}_{ij})r_{ij}^{-3}].$$

In the nonrelativistic limit, H_B separates out into parts that are easy to interpret.[6] Some of them produce effects that can be taken into account by changes in the electrostatic parameters (e.g., the parameters F^k, α, β, and γ for f^N). Into this category fall the retardation of the Coulomb interaction, the magnetic interactions between the electrons produced by their orbital motion, and the contact interaction between electron spins. Other parts produce effects that cannot be absorbed into the param-

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